Supporting Information for Polybenzimidazolium Salts: A New Class of Anion-Conducting Polymer

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General

All chemicals were obtained from Sigma-Aldrich Canada Ltd. 3,3’-diaminobenzidine and isophthalic acid were purified according to literature procedures. Deionized H_2O was purified using a Millipore Gradient Milli-Q® water purification system. ^{1}H NMR spectra were obtained using a Varian Unity Spectrometer operating at 500 MHz. The compounds were dissolved in DMSO-d_6 at a concentration of ~30 mg/mL. Fourier transform infrared spectroscopy (FTIR) was performed on a Bomem FTLA2000-154 FTIR system. Polymer films for FTIR analysis were drop-cast from dilute DMSO solution onto a glass slide and dried under vacuum at 80 °C for 2 h. Water uptake was determined by taking the mass difference between the wet and dry films (w_{wet} -w_{dry}) and dividing it by the dry film mass (w_{dry}) according to the equation below. Water uptake is reported as the average value measured for three similar samples.

$$WU = \frac{w_{wet} - w_{dry}}{w_{wet}} \times 100\% \qquad \text{(S1)}$$

For water volume uptakes, membranes were dried under vacuum at 80 °C for 24 h and their dimensions measured twice for each membrane - after drying and then again after soaking in deionized H_2O (DI H_2O) for 24 h at room temperature. Membrane thickness was measured with Series 293 Mitutoyo Quickmike callipers, while length and width were measured with Series 500 Mitutoyo Digimatic Calipers. VU was calculated using Equation S2:

$$VU = \frac{V_{wet} - V_{dry}}{V_{wet}} \times 100\% \quad \text{(S2)}$$

Water content (λ, moles H_2O per mole X^-) was calculated using water uptake (WU) the molecular weight of water (MW_{water}) and IEC using Equation S3:

$$\lambda = 10 \times \frac{WU}{MW_{water} \times IEC} \qquad \text{(S3)}$$

Anionic conductivity was measured by ac impedance spectroscopy with a Solartron 1260 frequency response analyzer (FRA) employing a transverse two-electrode configuration. Membrane samples were soaked in DI H_2O overnight, cut to required dimensions (0.5 cm × 1.0 cm), and laid across two Pt electrodes (1 cm × 1.5 cm) 0.5 cm apart, fixed on a PTFE block. A second PTFE block was placed on top and two clamps were used to hold the assembly together during measurement. Both PTFE blocks were vented with rectangular cut-aways to allow for membrane hydration. Membranes were kept hydrated by periodically wetting them with DI H_2O.

Ionic resistance was extracted from impedance data and fitting was performed by non-linear least squares regression analysis to a standard Randles equivalent circuit model. The ionic resistance was used to calculate anionic conductivity, σ_{X-}, according to Equation S4:

$$\sigma_{X-} = \frac{L}{R_m A} \qquad \text{(S4)}$$

where L is the spacing between the Pt electrodes (0.5 cm), A is the cross sectional area of the membrane (w × h), and R_m is the ionic resistance of the membrane.

Anion concentrations for the membranes were determined according to Equation S5:

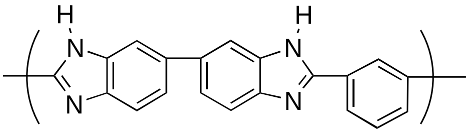
$$[X^-] = \frac{IEC \times w_{dry}}{V_{wet}} \qquad \text{(S5)}$$

The effective anion mobility was then calculated from Equation S6:

$$\mu'_{X-} = \frac{\sigma_{X-}}{F[X^-]} \qquad \text{(S6)}$$

where F is Faraday’s constant.

Synthesis of Polybenzimidazole, PBI (1)



1

Polymer **1** was synthesized using a literature procedure.[1] Polymer **1**: ^{1}H NMR (500 Hz, DMSO-d_6, δ, ppm) (Figure S1): 13.30 (2H, s, H_F), 9.18 (1H, s, H_D), 8.35 (2H, d, 1 Hz, H_A), 8.06 (1H, s, H_F), 7.70 (6H, m, $H_{B,C,E}$). The ^{1}H NMR spectrum (Figure S1) obtained for **1** was consistent with those found in the literature for similar materials. The peak found at 13.30 ppm is due to imidazole N-H protons and is in appropriate ratio with the aromatic region in the spectrum (i.e. integral of 2 H for the peak at 13.30 ppm and 10 H for the aromatic region from 9.17 - 7.70 ppm).

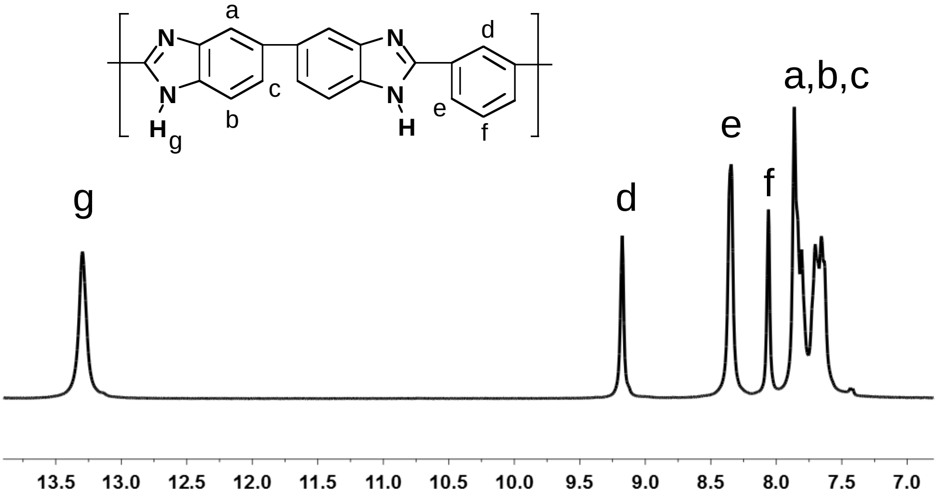


Figure S1. ^{1}H NMR spectrum of **1** showing proton assignments.

The FTIR spectrum for **1** (Figure S2) shows good agreement with results found in the literature. For example there is a broad absorbance at 2400 – 3600 cm^{-1}, which correlates to C-H and N-H stretching frequencies. As well there is a characteristic poly(benzimidazole) peak at 1287 cm^{-1} due to the imidazole ring breathing frequency.

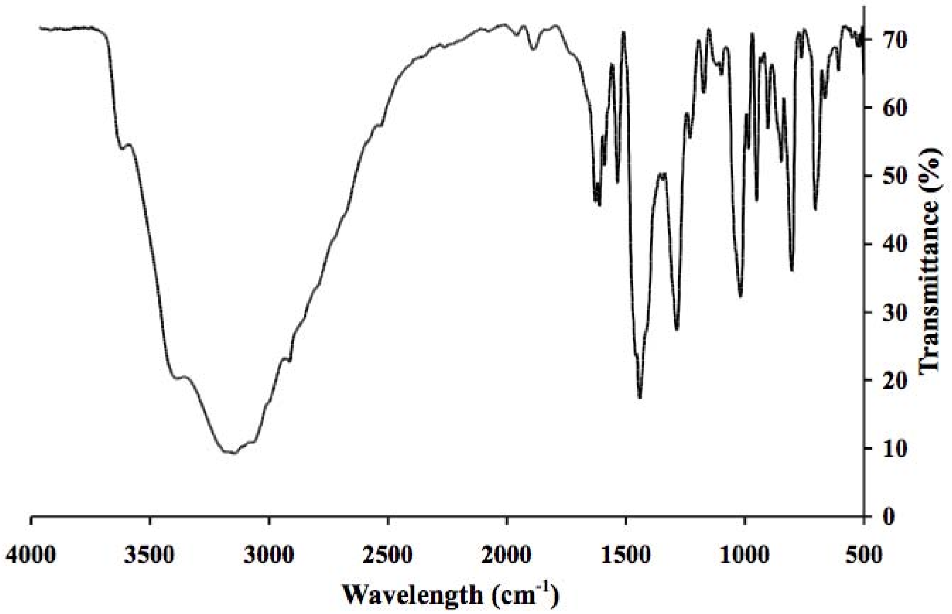
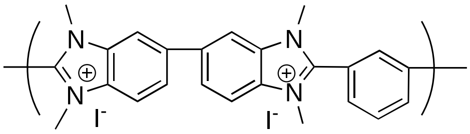


Figure S2. FTIR spectrum of **1** (film).

Synthesis of Poly(dimethylbenzimidazolium diiodide), P(DMBI) (2-I$^-$)



2-I$^-$

2-I$^-$ was made according to a modification of a literature procedure.[2] In a 250 mL round bottom flask, **1** (2 g, 6.5 mmol) was dissolved in dry NMP (100 mL). The flask was fitted with a condenser and placed under argon. The mixture was heated with stirring to 80 °C for 2 h until the solid had dissolved and was then allowed to cool to room temperature. LiH (0.3 g, 38 mmol) was then added slowly to the stirred solution. The temperature was increased to 80 ºC and stirred for another 15 h. The remaining LiH solid was removed by centrifugation. The decanted solution was returned to the round bottom flask and allowed to cool back to room temperature. Iodomethane (9 mL, 144 mmol) was added drop-wise over 15 min to the stirred solution. When the addition was complete, the reaction mixture was heated to 80 ºC and stirred for 6 h. The light brown solid that precipitated during the course of the reaction was isolated by vacuum filtration and then dissolved in DMSO (60 mL). Additional iodomethane (9 mL, 144 mmol) was added and the mixture then heated to 80 ºC for 15 h. After the cooling, the polymer was precipitated in acetone and residual DMSO was removed via Soxhlet extraction of the precipitated polymer (using acetone as extraction solvent) for 16 h. Polymer **2-I$^-$**: ^{1}H NMR (500 Hz, DMSO-d_6, δ, ppm) (figure S3): 8.84–8.26 (10H, aromatic protons, $H_{A\text{-}E}$), 4.23, 4.15 (11.89H, methyl protons $H_{G,H}$). Membranes of **2-I$^-$** were cast from DMSO solutions onto glass slides, heated to 60 ºC for 6 h and dried under vacuum overnight at 50 ºC. The films were removed from the slides by brief immersion in DI H_2O.

The ^{1}H NMR spectrum (Figure S3) for **2-I$^-$** was consistent with that found in the literature. The peaks found at 13.30 ppm in polymer **1** were absent in polymer **2-I$^-$**, signalling the removal of these protons. Also the spectrum had two new peaks at 4.23 and 4.15 ppm which are a result of the methylation. The degree of methylation was determined the ratio between the methyl peaks (4.23 and 4.15 ppm) and the aromatic peaks (8.84 - 8.26 ppm). The resulting degree of methylation was found to be 0.96 methyl groups per nitrogen or 96 % methylated.

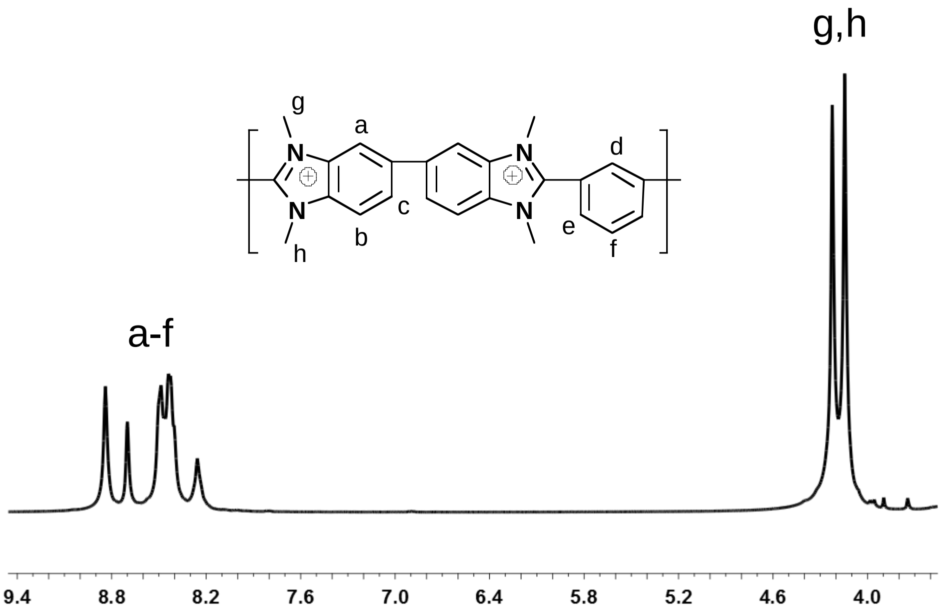


Figure S3. ^{1}H NMR spectrum of **2-I**$^-$.

FTIR analysis (Figure S4) showed a decrease (relative to the spectrum for **1**) in the absorbance around 3200 cm^{-1}, indicative of a reduction in the quantity of N-H bonds. The C-N stretch at ~1200 cm^{-1} was found to increase for **2-I**$^-$ relative to **1** due to an increase in the quantity of C-N bonds.

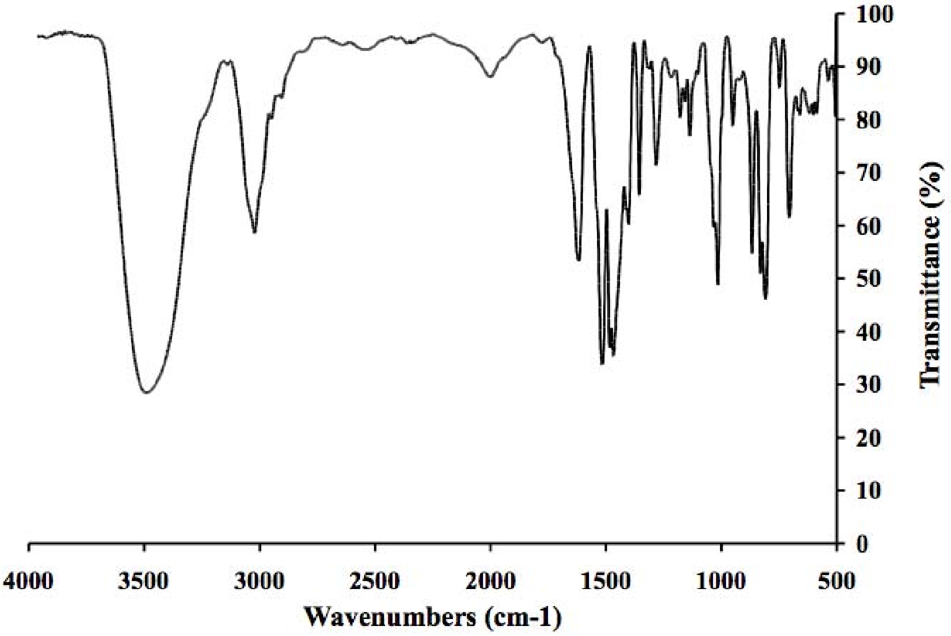
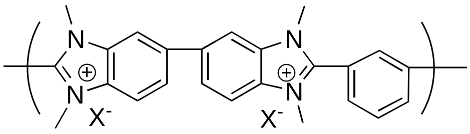


Figure S4. FTIR spectrum of **2-I$^-$** (film).

Anion Exchange (2-X$^-$ where X- = Cl$^-$, Br$^-$, NO_3^-, HCO_3^-)



2-X$^-$

X$^-$ = Cl$^-$, Br$^-$, NO_3^-, HCO_3^-

Films of **2-I$^-$** were soaked in 2 M KX (where X$^-$ = desired anion) for 24 h. The films were then soaked in DI H_2O for 4 h, refreshing the water frequently, followed by an overnight soak in DI H_2O. The membranes were then dried at room temperature.

To determine the degree of exchange, films of **2-X**$^-$ were soaked in 2 M KNO_3 overnight to release the counter ion from the membrane. The membrane was removed from solution and rinsed with fresh DI H_2O, and then dried overnight 80 ºC under vacuum and weighed to give the dry weight of the exchanged membrane. The rinse solution and the original KNO_3 solution were combined. To this solution was added a few drops of 0.1 M K_2CrO_4 as an indicator. The solution was then titrated with a standardized $AgNO_3$ solution until the endpoint (appearance of a red colour) was reached. The conversion percentage can be obtained from Equation S7.

$$\%Exchange = \frac{V_{AgNO_3} \times [AgNO_3]}{w_{dry} \times IEC_{2-NO_3^-}} \times 100\% \qquad \text{(S7)}$$

Water uptake and anionic conductivity values for **2-X**$^-$ (where **X**$^-$ = Cl^-, Br^-, I^-, NO_3^-, HCO_3^- and I_3^-) were carried out as described earlier and summarized in Table 1.

The complex plane plot (obtained using ac impedance spectroscopy) for **2-I**$^-$ for a membrane soaked in water is shown in Figures S5. A large drop in resistance is observed for a membrane going from a dry state to a wet state and thus it is clear that conductivity observed in the wet state is due to conduction of anions rather than electrons.

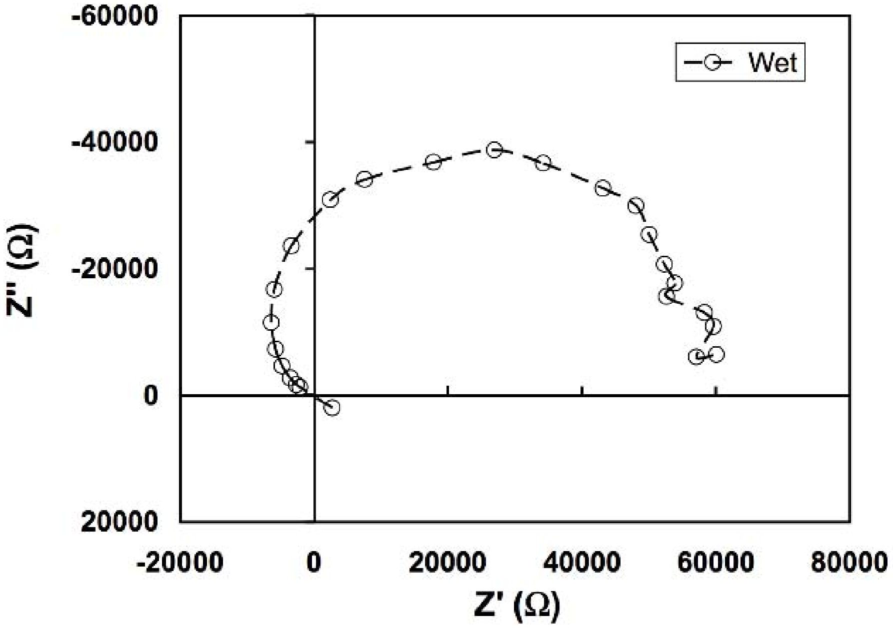
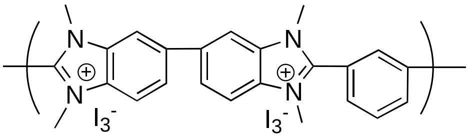


Figure S5. Complex plane plot of **2-I**$^-$ for a wet membrane obtained from ac impedance spectroscopy.

Anion Exchange (**2-X$^-$** where X- = I_3^-)



2-I_3^-

Films of **2-I$^-$** were soaked in I_2-saturated methanol (or acetonitrile) for 72 h. The membranes were then patted with a Kimwipe to remove any surface solvent and dried at room temperature for 24 h (or used as is in the case of acetonitrile as solvent). The same procedure was used for I_2-impregnation of films of **1**. I_2-uptake was calculated by subtracting the dry weight of the membrane before the addition of I_2 from the dry weight of the membrane after the addition of I_2.

Attempted exchange of I$^-$ with OH$^-$ for 2-I$^-$

Conversion of **2-I$^-$** to **2-OH$^-$** was attempted by soaking membranes of **2-I$^-$** in 2 M KOH. However, the resultant material was found to be very brittle in comparison with the original starting membrane. FTIR analysis indicates a reduction in the ring breathing mode of the imidazole ring, as well as a new absorbance at 1703 cm^{-1} which appears to indicate the formation of C=O containing functional group. These results suggest that decomposition and possible ring-opening of the imidazole moiety is occurring, resulting in possible cleavage of the polymer chain.

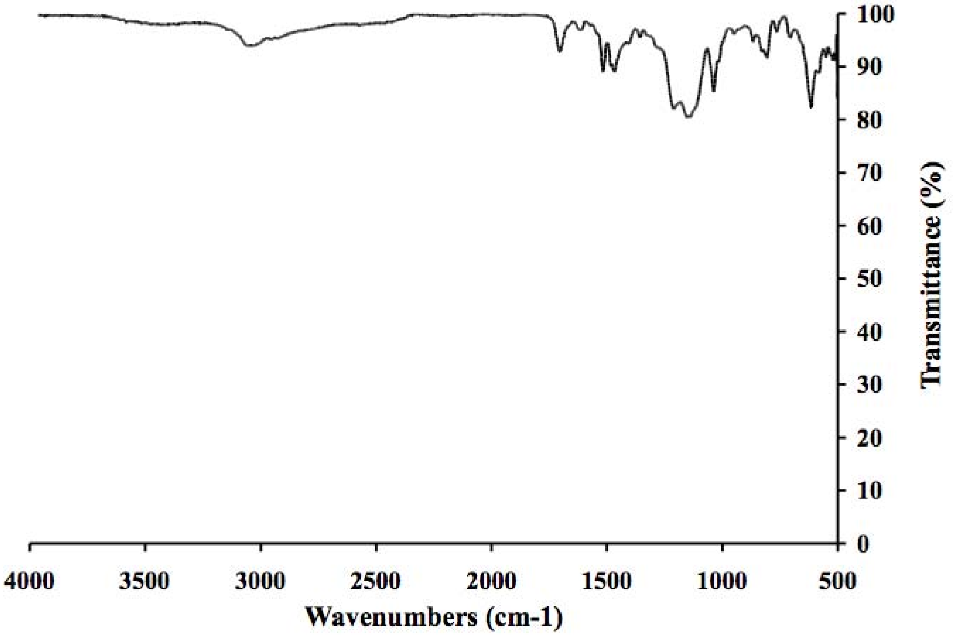
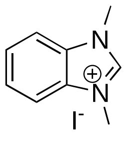


Figure S6. FTIR (KBr pellet) spectrum of **2-I$^-$** after treatment with strong base (KOH).

Synthesis of Dimethylbenzimidazolium iodide, DMBI$^+$I$^-$ (3-I$^-$)



3-I$^-$

In order to study the decomposition behaviour of **2-I$^-$** in the presence of strong base, a small molecule analogue (**3-I$^-$**) was synthesized. Benzimidazole (1.0 g, 8.5 mmol) was dissolved in 30 mL acetone. Powdered KOH (2.5 g) was added while stirring rapidly. Methyl iodide (5 mL, 80 mmol) was added drop-wise to the stirred solution. The reaction mixture was then stirred at room temperature for 2 days. The white solid was filtered and washed with acetone, and dried under vacuum. The ^{1}H NMR (Figure S7) and FTIR (Figure S8) spectra were consistent with the assigned structure. ^{1}H NMR (500 Hz, DMSO-d_6, δ, ppm) (figure S5): 9.71 (1H, H_D), 8.03 (2H, m, 3 Hz, H_B), 7.70 (2H, m, 3 Hz, H_A), 4.09 (6H, s, methyl protons, H_C).

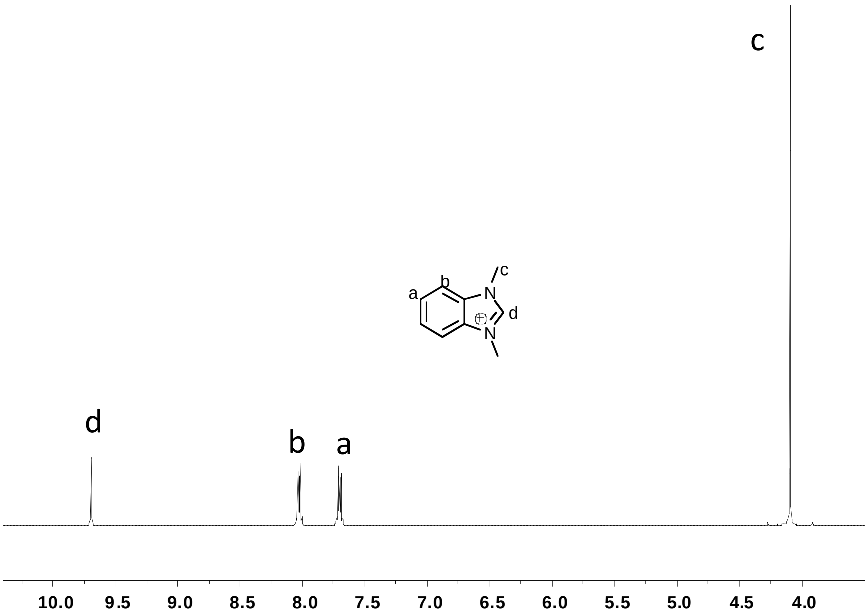


Figure S7. ^{1}H NMR spectrum of **3-I**$^-$.

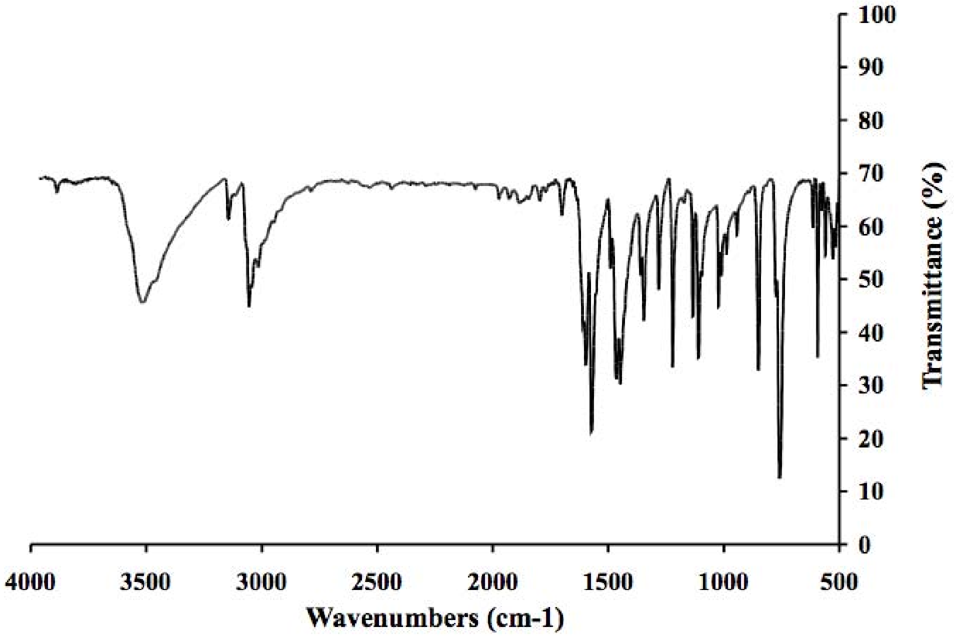
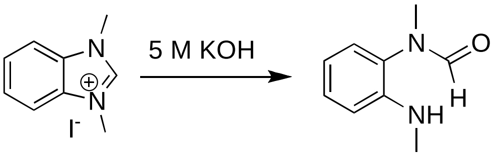


Figure S8. FTIR (KBr pellet) spectrum of **3-I$^-$**.

Decomposition product of 3-I$^-$ in presence of OH$^-$



3-I$^-$ **4**

To a solution of **3-I$^-$** (0.5 g) dissolved in DI H_2O (4 mL) was added 4 mL of 5 M KOH. The solution was stirred for 24 h and two layers formed. The mixture was extracted with ether (5 mL) and the aqueous layer was separated and dried over $MgSO_4$. The ether was removed by evaporation yielding a white powder. ^{1}H NMR (Figure S9) and FTIR (Figure S10) spectra were consistent with the assigned structure (**4**). ^{1}H NMR (500 Hz, DMSO-d_6, δ, ppm): 7.98 (1H, H_H), 7.21 (1H, m, H_B), 6.99 (1H, m, 3 Hz, H_D), 6.62 (2H, m, $H_{A,C}$), 6.62 (1H, q, 4 Hz, H_G), 3.00 (3H, s, H_F), 2.70 (3H, d, 4 Hz, H_E).

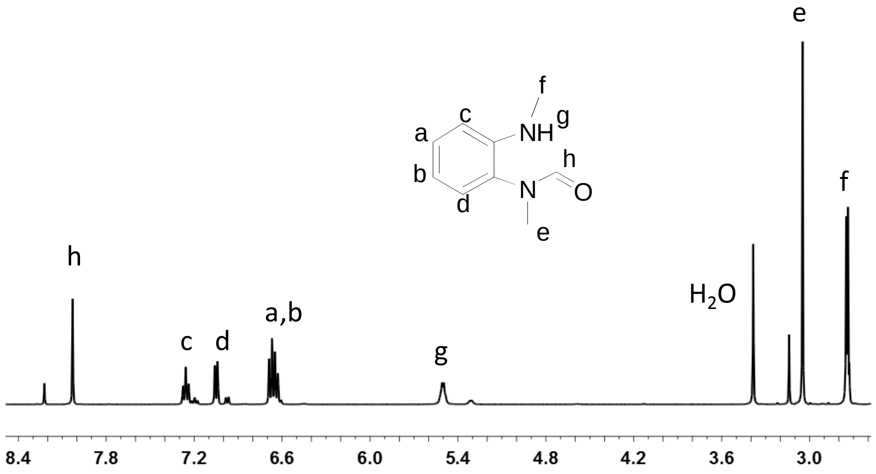


Figure S9. ^{1}H NMR spectrum of **4**.

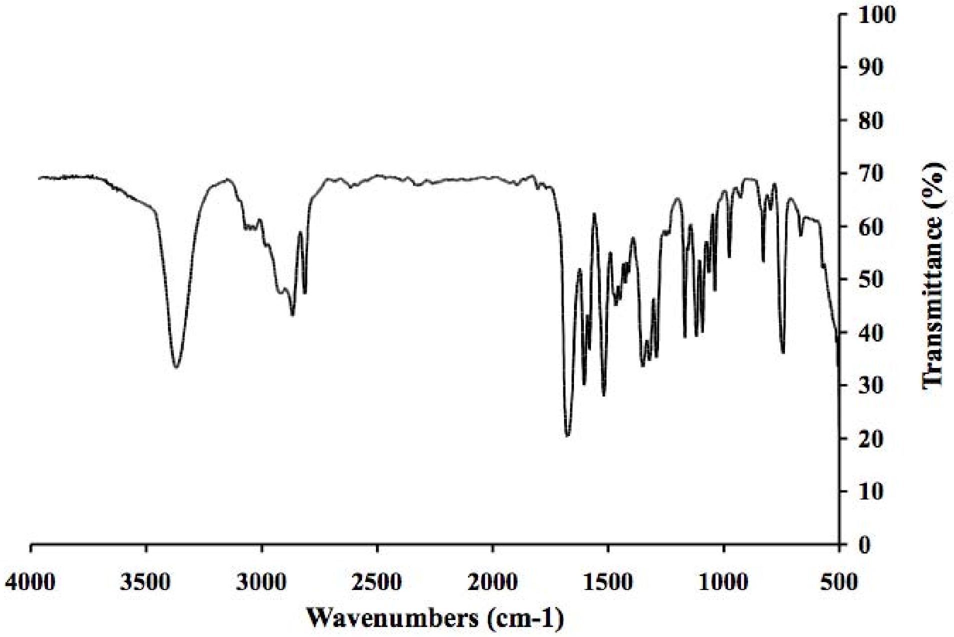


Figure S10. FTIR spectrum of **4** (KBr pellet).

References

(1) Kulkarni, M.; Potrekar, R.; Kulkarni, R. A.; Vernekar, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5776.
(2) Hu, M.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 553.